

To: Christopher Johnson, P.E.
Associate Vice President
Project Manager
Carollo Engineers, Inc.
12592 W. Explorer Dr., Suite 200
Boise, ID 83713

Re: Preliminary Analysis of Fresno Corrosion Issue and Recommendations (Draft)

9/1/2016

Dear Christopher,

Over the last few months I have reviewed water quality data, prior consulting reports and experiences associated with the Fresno galvanized iron corrosion issue. I have also been provided extensive data, analysis and insights from Thomas Esqueda (Fresno Director of Public Utilities). This report provides background into the nature and possible cause(s) of the problem, and recommends steps to mitigate the corrosion concerns.

Although this must be considered a preliminary analysis, given the significant effort that is already underway at Fresno to better understand the situation, at this time I draw the following conclusions.

- 1) The Major Concern is Galvanized Iron Corrosion: Red Water, Scaling and Lead
- 2) While the EPA Lead Action Level Has Not Been Exceeded, More Testing Is Warranted
- 3) Fresno is the First of Many Californian Cities Who Will Deal With This Issue
- 4) Scientific Understanding is Poor: Corrosion of GI-pipe is Unpredictable
- 5) Monitoring Consumer Observations and Complaints is Critical
- 6) GI-Pipe Corrosion Control and The Utility Response Can Be Improved

1) The Major Concern is Galvanized Iron Corrosion: Red Water, Scaling and Lead

Galvanized Iron Pipe (GI-pipe) has not been a preferred plumbing material for water service lines or premise plumbing in the United States for several decades. Galvanized iron pipe is made of steel (iron), with a thin protective coating of zinc that can also contain up to 1-3% lead by weight. Its satisfactory performance has always been critically dependent on the chemistry of potable water. Historically, some potable waters have been found to cause low corrosion rates for GI pipe, whereas other waters caused very serious problems that included white water (zinc particles), red water (iron rust), pipe blockage, leaks due to pitting corrosion, or elevated lead from the coating.

When the plumbing code of most cities was established, local experience regarding pipe corrosion in the local water supply was considered in terms of the recommended pipe materials. The water supplies in which excessive corrosion of galvanized iron were known to occur, more quickly developed codes that required more corrosion resistant materials such as copper or plastics, but cities with a less corrosive water supply have continued to allow less expensive galvanized iron plumbing to the present day.

If a change in water supply or pipe configurations occurs, historically satisfactory performance of GI-pipe can immediately become unsatisfactory. For example, in the 1970s many Californian cities began to install copper service lines, which triggered very rapid failure of the GI-pipe in homes due to copper deposition corrosion. Essentially, the copper ions released to water, dramatically accelerated the corrosion and failure of the GI-pipe. In other situations, cities have changed their water supply from a non-corrosive to corrosive source for GI-pipe, and immediately triggered widespread problems. An illustrative high profile GI-pipe corrosion problem occurred in Tuscon AZ during the early 1990s, after a switch from non-corrosive groundwater to more corrosive surface water.

Many of the corrosion problems reported in Fresno over the last decade, can be attributed to GI-pipe that performed satisfactorily on groundwater, and which experienced worse problems after switching to a more corrosive surface water source.

2) While the EPA Lead Action Level Has Not Been Exceeded, More Testing Is Warranted

Fresno maintains an EPA lead and copper rule sampling pool, and sampling of those homes has not indicated any lead in water problems. However, none of the tested homes have GI-pipe, because EPA has not traditionally considered GI-pipe a significant risk factor for elevated lead in water.

GI-Pipe could be a modest risk factor for higher lead in Fresno cold drinking water. Using data provided by Fresno for samples collected predominantly from hot water, there is a moderate correlation ($R^2 = 0.54$) between lead and zinc in water (Figure 1). The slope indicates that in a typical home, lead released to water will be about 3% of the Zn released to water by weight. This is roughly consistent with the ratio of lead to zinc found in GI-pipe coating. Iron was also weakly correlated with lead ($R^2 = 0.23$), which is also consistent with a GI-pipe source.

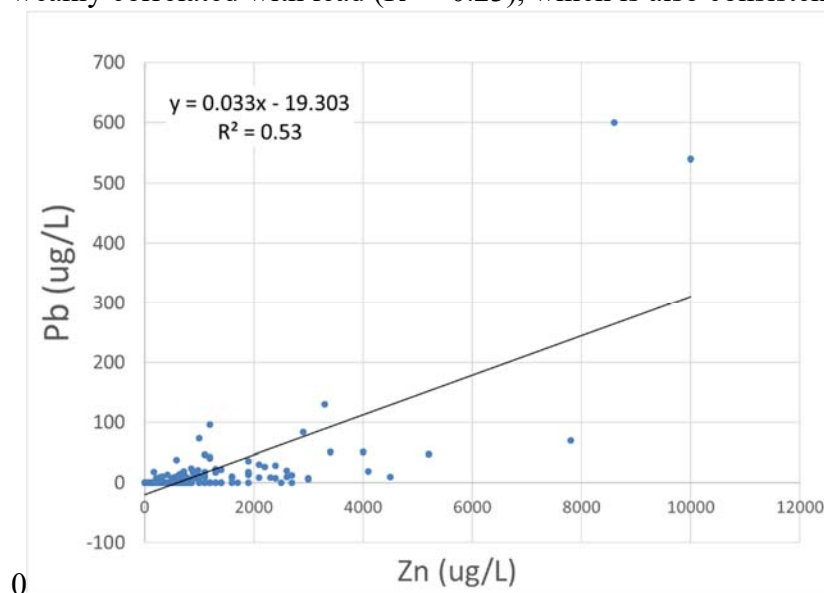


Figure 1. Moderate correlation between Pb and Zn in Fresno water samples. The slope of 0.033 indicates that in a typical home, lead will be about 3% of the zinc content.

Presently, only four samples from kitchen taps in Fresno have exceeded the 15 ppb EPA lead action level. Water from showers or tubs are not acceptable for determining compliance with EPA standards, because the fixtures at those locations tend to have sub-standard brass that has elevated lead, and those fixtures were not designed to dispense potable water fit for human consumption. Likewise, hot water sources are never tested for compliance with EPA lead in water standards, [because we assume hot water tends to have higher lead, and therefore EPA recommends that hot water not be used for drinking or cooking.](#) The vast majority of taps testing above the action level for lead in Fresno, have not been from cold water kitchen sources. Hence, the extent of the problem with lead in cold potable water is unclear. On the basis of EPA LCR monitoring, it would appear that lead levels in cold kitchen water are well within the existing law.

Very serious lead in water problems, can sometimes occur when GI-pipes are installed after a lead pipe in the flow sequence. Over decades of use, the iron on the GI-pipe can adsorb (i.e., sponge up) very high amounts of lead from the lead pipe. Lead pipes have reportedly not been used in Fresno, so the very serious problems reported with lead from GI-pipe in Flint or Washington D.C. homes (these homes also tended to have lead pipe) are not expected in Fresno.

I have recommended that the city revisit homes with prior high water lead testing results, and resample them from the kitchen cold water line to determine if there is a problem with drinking water in Fresno homes with GI-pipe. In the unlikely event such problems are observed, special public health warnings should be provided to residents of those homes, as was the case in Washington D.C..

3) Fresno is Likely the First of Many Californian Cities Who Will Deal With This Issue

The Sustainable Groundwater Management Act (SGMA) will cause many California utilities to consider either switching/supplementing existing groundwater sources with new surface water sources. While surface water is not inherently more corrosive than groundwater, anytime a change in water sources occurs, there is a significant risk of triggering problems with GI-pipe corrosion.

4) Scientific Understanding is Poor: Corrosion of GI-Pipe Is Unpredictable

Because GI-pipe is not considered a preferred modern pipe material, very little research has been done to determine what makes a water non-corrosive and what makes a water corrosive for GI-pipe. The general attitude is that when GI-pipe corrosion problems are encountered, the antiquated pipe material should be replaced with more corrosion resistant materials, or the pipe should be cleaned and then lined with epoxy. But in cities such as Fresno where GI-pipe has performed satisfactorily over the years, there is a large capital investment in this infrastructure, that may make pipe replacement impossible.

The corrosion performance of GI-pipe is further complicated by many factors. First, GI-pipe surfaces can range from 100% zinc in new pipe, to 100% iron in very old pipe, and everything in

between those extremes as the pipe ages. GI-pipe behaves differently at every stage of its aging process. Second, corrosion indices and models cannot predict what cold waters are corrosive and what waters are non-corrosive to GI-pipe, because current understanding is so poor. As noted previously, having even a small upstream brass or copper component, can accelerate corrosion of GI-pipe dramatically. Finally, amongst all the plumbing materials, GI-pipe can have the greatest discrepancy between hot and cold water performance due to a phenomena known as “electrochemical reversal.”

In a normal situation, the zinc coating is anodic relative to iron, and as a result the zinc coating protects the pipe and extends its life and corrosion resistance. However, in some hot waters, electrochemical reversal occurs, which can cause the zinc coating to actually attack the underlying iron (Appendix B). In these cases the pipe essentially self-destructs. The net result is that some cold waters which are highly non-corrosive to GI-Pipe, become extremely corrosive to GI—Pipe when heated. Anecdotally, it has been reported that many hot water GI-pipe systems in Fresno have been attacked or experienced corrosion problems, suggesting that electrochemical reversal or copper deposition corrosion may be playing an important role.

This discussion illustrates the numerous challenges associated with maintaining a large GI-pipe infrastructure, and why GI-pipe is no longer considered a suitable material for most potable water systems.

5) Monitoring Consumer Observations and Complaints is Critical

Because corrosion is so poorly understood, and consumers are on the front lines experiencing corrosion problems that have important aesthetic and public health implications, it is critically important that cities carefully monitor and respond to all consumer complaints. For example, the “The Recommended Standards for Water Works,” or “Ten State Standards”, first published in 1953, includes a section on corrosion control that was adopted in 1982. The Standard guides water utilities on the subject of internal corrosion, and mentions the need for a system of record keeping and mapping of internal corrosion problems, and specifically requires water utilities to follow up with an inspection of customers’ properties by experienced personnel or a consultant experienced in corrosion control when complaints are received.

Where advisable, water utility companies also are required to obtain samples of water for chemical and microbiological analyses and plumbing material samples in order to determine the cause of the corrosion. If internal corrosion problems are noted throughout the system, the water should be modified at the treatment plant, pump station or well head. Other standards such as the American Water Works Association report “Distribution Systems Operation and Management,” similarly states that the utility shall evaluate customer inquiries related to water quality, including those relating to corrosion concerns, and shall implement a plan to investigate and respond to those inquiries.

Clearly, Fresno did not adequately monitor or respond to consumer complaints over the last ten years, which has created understandable frustration amongst consumers, and it has also delayed identification and solution of GI-pipe corrosion problems by the city.

6) GI-Pipe Corrosion Control and The Utility Response Can Both Be Improved

The current director of public utilities, Thomas Esqueda, has been very proactive in identifying and responding to the GI-pipe corrosion problems. Continued aggressive action is important to ensure that the existing problems are ameliorated, and that future problems associated with the new surface water treatment plant will be avoided to the extent that is possible. Two areas of activity are especially important.

A. Continue Working Closely With Fresno Consumers

Fresno should implement a customer service and response program, consistent with *"The Recommended Standards for Water Works."* Moreover, a testing program should be initiated, in order to better understand the corrosion of GI-pipe, in both hot and cold water. The program should include sites that are exclusively on groundwater, exclusively on surface water, and those that are in mixing zones where the water sources changes between the two. Homes with prior consumer complaints should be the highest priority for testing. Water heater sediment should be examined for scale deposits, and representative samples of hot and cold water GI-pipe should be extracted and examined. Customers should be queried as to whether and when their GI-pipes have failed.

B. Optimize Corrosion Control Using Bench or Pilot Testing

The overall system corrosion control strategy needs to be harmonized, to meet EPA LCR goals, GI-pipe corrosion control, and hot water scaling control. In general, approaches mixing waters with different control strategies, such as phosphate based corrosion control versus pH-alkalinity corrosion control, should be avoided.

An array of simple bench tests with conditions examining the prior corrosion control strategy used at the surface water treatment plant, the current corrosion control strategy with extra lime, and other projected strategies should be conducted. Both cold and hot water should be tested. Parameters to be evaluated should include scaling, electrochemical reversal, GI-pipe corrosion rate as determined by the rate of oxygen consumption and metal release (Pb, Zn, Fe).

I hope you find these comments valuable as you plan your future activities. If you should have any questions, please contact me at 540 320-8740 or via email at edwardsm@vt.edu.

Sincerely,



Dr. Marc Edwards
Consultant

Appendix A. Lead Release to Drinking Water from Galvanized Steel Pipe

Coatings

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ABSTRACT

Problems identified with elevated lead in drinking water associated with galvanized steel pipe were recently hypothesized to result from lead accumulation on galvanized steel pipe surfaces from upstream lead service pipes. However, historical research documents that the grade of zinc typically used for galvanizing contains a minimum of 0.5% lead and can itself be a significant long-term source of lead, which may explain some recent lead contamination problems associated with galvanized steel. Surface analysis of various galvanized steel pipes and fittings installed from 1950-2008 demonstrated that the concentration of lead in the original zinc coating can range from non-detect to nearly 2%, dependent on manufacturer and fitting type. Since cadmium is also present in many zinc coatings, but not in lead pipe, leaded solder, or brass, correlation of zinc concentration to both lead and cadmium concentrations in water was considered as a possible “fingerprint” implicating the coating on galvanized steel as a lead source; bench scale tests of metal leaching from harvested galvanized steel pipes were used to validate this approach. Using profile sampling, individual homes with galvanized steel pipe as a primary lead source were identified in Washington, D.C., Providence, RI, Chicago, IL, and a city in Florida. In some cases the levels of lead from this source were very significant ($> 100 \mu\text{g/L}$)

and can be exacerbated by installation of copper pipe upstream during partial service line replacements.

INTRODUCTION

Exposure to lead in water remains a significant public health concern and is receiving increased attention as other sources are addressed and public health goals become more stringent (Shannon and Graef 1989; Triantafyllidou and Edwards 2011; Deshommes et al. 2013; Etchevers et al. 2014; Triantafyllidou et al. 2014). Historically, lead pipes, leaded solders, and lead-containing brass and bronze have been considered the dominant sources of water lead, and continue to dominate lead release in many homes, although galvanized steel pipes have been acknowledged to be significant in some cases (Korshin 1999; Triantafyllidou and Edwards 2011). In this work, the term “galvanized steel pipe” refers to a steel pipe coated with sacrificial zinc coating, which may contain lead, and the term “zinc coating” refers to the zinc layer only.

Zinc Coating as a Source of Lead. Although galvanized steel pipes have fallen out of favor in the U.S., they were the most commonly installed pipe material for most of the 20th century (AWWA 1996) and are still installed in some present-day buildings. In a large national water utility survey, 52% of utilities (N = 898) reported the presence of steel or galvanized steel service lines within their distribution system, and an estimated 7.5% of households overall had steel or galvanized steel services (American Water Works Association 1996). The source of lead in galvanized steel pipes is the zinc coating. It is common practice to use Prime Western Grade zinc in galvanizing baths (AWWA 1996), which contains a *minimum* of 0.5% lead by weight and a maximum of 1.4% lead by weight (AWWA 1996; ASTM 2013a; ASTM 2013b). While galvanizing can be accomplished using other grades of zinc containing lower levels of lead, the presence of lead in the galvanizing kettle has processing advantages, including increased fluidity

(American Galvanizers Association 2006). In comparison, the level of lead in “lead free” components for potable water use was recently reduced to a maximum of 0.25% in the wetted surface material (United States Environmental Protection Agency 2012), making the level of lead found in many zinc coatings unacceptable for potable use if judged by the new standard. When lead is present in the zinc coating, it can be released to water either in soluble form through dissolution of the zinc coating or in particulate form through the scouring of zinc corrosion products at high flow rates (Figure 1a). In this work, this is referred to as *direct* lead release.

Cadmium as a Fingerprint for Galvanized Steel Pipe. In situations where lead release is dominated by dissolution of zinc coatings, it is expected that lead and zinc concentrations will tend to be correlated. However, several attempts to study lead release from galvanized steel pipe have been confounded by the presence of brass fittings (Neff et al. 1987; Lee et al. 1989), which also contain both lead and zinc. One possible way to distinguish lead from galvanized steel and lead from brass in the field is by using the cadmium concentration as a “fingerprint.” Prime Western Grade zinc can contain up to 0.2% cadmium (AWWA 1996; ASTM 2013b), and bench scale experiments under intermittent flow conditions have demonstrated that the concentrations of zinc, cadmium, and lead released from galvanized steel pipes can correlate with each other (Meyer 1980). Such correlations between lead and cadmium release were successfully used in Poland to identify galvanized steel as a water lead source (Barton et al. 2002; Barton 2005).

Other Sources of Cadmium in Drinking Water. According to EPA, the primary sources of cadmium in drinking water are the corrosion of galvanized pipes, erosion of natural deposits, discharge from metal refineries, and runoff from waste batteries and paints (United States Environmental Protection Agency 2013). Other than galvanized steel pipe corrosion, these

major sources of cadmium are expected to affect the cadmium concentration in the source water, which can be identified by taking samples for cadmium at the treatment plant or checking the cadmium concentration of well-flushed field samples. Brass tends to have only traces of cadmium relative to lead (e.g., Schock and Neff 1988). In the field, the amount of cadmium released from galvanized steel pipe has been sufficient to distinguish it from other materials despite possible confounding factors; in Seattle, homes with galvanized steel pipe had cadmium concentrations at least ten times higher than homes with copper pipe (Sharrett et al. 1982).

Galvanized Steel Pipe as a Direct Lead Source. A literature review identified numerous laboratory and field studies (Table 1) demonstrating that galvanized steel pipe can be a significant source of lead in drinking water (McFarren et al. 1977; Center for Disease Control 1978; Meyer 1980; Lee et al. 1989; AWWA 1996; Quevauviller and Thompson 2005; Lasheen et al. 2008). Experiences with samples in France found that lead concentrations from galvanized steel are typically below 10 µg/L, but can frequently reach 25 µg/L and are sometimes as high as 100 µg/L (Quevauviller and Thompson 2005). Similarly, data taken from homes with galvanized steel pipe in Portland, OR showed a median lead level of 10 µg/L and a 90th percentile value of 20 µg/L (AWWA 1996). These data imply that pre-2014 galvanized steel could contribute enough lead to create problems with action level compliance and human health (Triantafyllidou et al. 2014). It is expected that the levels of lead released from galvanized steel pipe will tend to decrease as the zinc coating is depleted; however, one three-year intermittent-flow study demonstrated that lead can be released above the action level for at least several years after installation (Meyer 1980).

Galvanized Steel Pipe as an Indirect Lead Source. Recent work identified problems with elevated lead in homes with galvanized steel in Washington D.C. and concluded that the lead

present on the old galvanized steel pipe surfaces originated from upstream lead pipes (Sandvig et al. 2008; HDR Engineering Inc. 2009; McFadden et al. 2011), causing other researchers to draw similar conclusions when galvanized steel is serving as a source of lead in water (Deshommes et al. 2010). Conceptually, this mechanism is the result of the strong tendency for iron to adsorb lead; these iron scales can form on the galvanized steel pipe surface once the zinc coating has been lost (Figure 1b). If lead-rich iron scales form, they can serve as a reservoir for *indirect* release of lead from galvanized steel pipe, even once the original lead source has been removed. The mechanism was supported by surface analysis of iron scale scrapings from harvested galvanized steel pipes, which identified lead-rich regions within the iron scale; the authors stated that the zinc layer was no longer present in these pipes and did not consider its possible contribution to lead release (HDR Engineering Inc. 2009; McFadden et al. 2011). It was further acknowledged that the “seeding” of lead from services on downstream galvanized steel is a complex process dependent on pipe age, mineralogy, and water chemistry, particularly the presence of phosphate corrosion inhibitors (HDR Engineering Inc. 2009; Wasserstrom 2014), which implies that it may not occur universally to a significant extent when lead is present upstream of galvanized steel pipe. For example, HDR’s attempt to deposit lead on unlined iron tubing in a pipe loop setup led to weak adherence of lead to iron, with only 25% adhering to the surface, and half of this desorbing in the first week without lead dosing (2009).

Role of Deposition Corrosion. Deposition corrosion can occur whenever ions from a more noble metal (e.g., copper(I) and copper(II) ions) are present in water that contacts a less noble pipe material (e.g. lead or galvanized steel), form micro galvanic cells on the pipe surface, and dramatically accelerate corrosive attack, failure rates, and metal release (Kenworthy 1943). Most study of deposition corrosion has focused on the galvanized steel / copper system, and

practical experiences with devastating consequences have led to recommendations against the installation of copper before galvanized steel in the flow sequence and general guidance to avoid installation of more noble metals before less noble metals in the pipe flow sequence (Cruse 1971; AWWA 1986; NACE 1995). Nevertheless, the practice continues, particularly in large buildings and when lead service lines are partially replaced with copper in homes with galvanized steel premise plumbing (HDR Engineering Inc. 2009; Noble 2013). In the case of lead release from galvanized steel pipe, the presence of upstream copper is expected to accelerate lead release in both the direct and indirect cases of lead release from galvanized steel pipe (Figure 1c).

Objectives. The overall goal of this work was to re-examine the role of galvanized steel as a lead source in modern homes, schools, and large buildings. Specifically, this work examined (1) the concentration of lead on the surface of galvanized steel pipes of various ages and types, (2) the level of lead released to water from galvanized steel pipe in well-controlled bench-scale studies, and (3) the use of cadmium as a “fingerprint” to detect galvanized steel pipe as a source of lead in both homes and schools.

MATERIALS AND METHODS

Pipe Coating Analysis. The concentration of lead on the surface of the galvanized steel pipes was measured using a handheld x-ray fluorescence (XRF) analyzer (Innov-X Alpha 800 LZ). The measurement time for each XRF reading was 45 seconds. Unless noted otherwise, readings were taken on the clean outside surface of the pipe and represent the concentrations in the zinc coating before exposure to water. To confirm XRF results, sections of scale were removed from one set of pipes and digested using a mixture of nitric acid and hydroxylamine hydrochloride and analyzed for total metals by inductively coupled plasma – mass spectrometry (ICP-MS; Thermo

Scientific Thermo Electron X Series) using Standard Method 3125B (APHA 1998).

Bench Scale Study. Galvanized steel pipes (3/4" diameter) were harvested from a distribution system in Florida and cut into 6" sections. Twenty pipes were exposed to finished water from the city's treatment plant using a dump-and-fill protocol with water changes three times per week (MWF). During week one, no disinfectant residual was present; for the remaining weeks, free chlorine was added to a concentration of 2.1 mg/L to match the disinfectant residual measured leaving the treatment plant at the Florida utility. Water changes continued for three weeks, and samples were collected as weekly composites for each pipe. All samples were digested in the bottle by adding 2% trace metal grade nitric acid and 0.1% hydroxylamine hydrochloride, with a minimum of 24 hours of digestion at room temperature and 24 hours of digestion at 50 °C before analysis. Samples were analyzed for total metals by ICP-MS as above.

Household Sampling. Except for the data collected in the case of a child's elevated blood lead (EBL), all household samples were collected as part of sequential (profile) sampling using the protocol outlined in (Clark et al. 2014). At the sites in Washington D.C. and Chicago, IL, sequential profiles were collected at a low flow rate of 1 L/min with the aerator on, the highest possible flow rate with the aerator on, and the highest possible flow rate with the aerator off. Samples collected in Florida included only the two profiles with the aerator on. For the EBL case study, both first draw and 45 second flush samples were taken according to the standard EPA protocol (United States Environmental Protection Agency 1991; Triantafyllidou et al. 2012) at normal household flow rates with the aerator on at all taps in the home. All samples were acidified with 2% trace metal grade nitric acid and analyzed for total metals using the same ICP-MS method outlined above.

School Sampling. Samples in schools were collected according to the protocol outlined by EPA for voluntary monitoring in schools (United States Environmental Protection Agency 2006), which involves collecting a 250 mL sample rather than the 1 L sample typical in residential sampling. After overnight stagnation, both first draw and 45 second flushed samples were collected at all taps in the school used for drinking.

RESULTS AND DISCUSSION

After assessing the extent to which modern (pre-2014) galvanized steel pipes used in potable water systems contain lead, bench and field studies from a case study of a Florida utility with instances of elevated lead from galvanized steel service lines are reviewed. Results from a home in Chicago explored the effect of flow rate on lead release from galvanized steel pipe and confirmed the presence of cadmium as a “fingerprint” for lead derived from galvanized steel pipe coatings. This is followed by field results from home profile sampling, school sampling, and sampling in the EBL case study, demonstrating widespread significance of galvanized steel pipe as a lead source when it is present.

Concentration of Lead in Galvanized Steel Pipe Coatings. Significant concentrations of lead up to 1.8% were measured in the zinc coating of galvanized steel pipes and fittings (Figures 2,3). In 60-year-old galvanized steel service lines harvested from a distribution system in Florida, the coating on the outside of the pipe after surface cleaning contained 0.8 – 1.7% lead by weight (Figure 2). To put the amount of lead available for release from galvanized steel service lines in context, a calculation of “effective lead surface area” was performed for a representative household plumbing system with a galvanized steel service line and compared to a representative

mix of 6 brass utility service parts commonly found in home plumbing (as described in Maas et al. 2002).

For galvanized schedule 80 steel pipe, the surface area was calculated for a 25 ft, $\frac{3}{4}$ " service line and multiplied by 1.4%. For brass, the total surface area was estimated using volumes from the literature (Maas et al. 2002) and a surface area to volume ratio of $0.008 \text{ in}^2/\text{mL}$ (Triantafyllidou and Edwards 2007), which was then multiplied by the percentage of lead to give the effective lead area. The effective lead area was 63 cm^2 for the galvanized steel service line, whereas the range of effective lead areas was only $0.03\text{-}1.1 \text{ cm}^2$ for brass with lead levels from 0.25%- 8% lead.

From a different perspective, the total mass of lead in the galvanized steel service line would be $3.4 - 11.2 \text{ g}$ over the range of coating thicknesses documented in the literature (Fox et al. 1983), compared to $100 - 300 \text{ g}$ estimated to be available in pre-2014 lead-free brass (Triantafyllidou and Edwards 2011). A key implication of these calculations is that for galvanized steel pipe, a relatively small mass of lead is concentrated in the area contacting the water via the thin zinc coating, causing a disproportionate impact. For example, 11.2 g of lead is sufficient to contaminate an entire four-person household's daily water use (100 gal/day) to the $15 \text{ }\mu\text{g/L}$ action level for more than five years, if it was all released uniformly over that period.

For galvanized steel premise plumbing installed from 1990-2008, lead concentration varied significantly by manufacturer and fitting type (Figure 3). In large (10-12") diameter galvanized steel pipes installed between 2005 and 2008 in a large public building in Indiana, lead concentrations on the outside of the pipe measured by XRF ranged from non-detect to 1.8% (Figure 3a). Dissolution and ICP-MS analysis of scale harvested from the inside of the same pipes was consistent with XRF results, with lead/zinc ratios ranging from ND – 2.2%. Using this

more sensitive technique, for which the method detection limit (MDL) in the dissolved sample was 0.1 µg/L, cadmium was detectable in 5 / 18 samples, and was highest when lead was highest, implying that cadmium can serve as a positive indicator of galvanized steel pipe as a lead source, but that lead contributions from galvanized steel cannot be ruled out in the absence of cadmium. Similarly, in 1990s household plumbing harvested from a home in Chicago, lead concentrations on the outside of the pipe ranged from non-detect to 1.4% (Figure 3b). These results are consistent with expectations based on the use of Prime Western Grade zinc, which contains 0.5 to 1.4% lead, in the galvanizing process by some manufacturers (AWWA 1996; ASTM 2013b). The measurement of concentrations lower than 0.5% implies that some manufacturers used other grades of zinc for galvanizing. The measurement of concentrations higher than 1.4% is consistent with the fact that XRF is a surface-sensitive measurement technique, and impurities, such as lead, are known to concentrate in the (eta) layer of zinc, furthest from the underlying steel (AWWA 1996).

Lead Release from Galvanized Steel in Florida. Exposure of sections of the harvested 60-year-old Florida service lines described above to finished water during bench-scale tests demonstrated that the zinc coating can contribute significant lead levels to water. During a three-week dump-and-fill study, the concentration of lead in water reached a maximum concentration of 172 µg/L, more than ten times the EPA action level. Throughout the test, the ratio of lead/zinc in water was similar to the ratio of lead/zinc expected in the zinc coating, ranging from 0.2 – 1.5% with an average of 0.5%. When lead concentration is plotted as a function of zinc concentration, the two metals are correlated with $R^2 = 0.46$ (Figure 4a). A relatively strong correlation is also present between zinc and cadmium with $R^2 = 0.69$ (Figure 4a). For both lead and cadmium, the sample with the highest zinc concentration has a large effect on the linear fit; if this point is

excluded, the R^2 values change to 0.34 for lead and 0.77 for cadmium. If lead and cadmium are plotted against one another (Figure 4b), a moderate correlation with $R^2 = 0.44$ is observed. As expected based on the composition of Prime Western Grade zinc, the concentrations of cadmium are lower than lead (maximum cadmium = 13 $\mu\text{g/L}$; average cadmium/zinc = 0.05%). Despite the low concentrations, the relationship between the concentrations of zinc, lead, and cadmium provided further support for the use of cadmium as a “fingerprint” element for the presence of galvanized steel pipe.

Field sampling in the same city in Florida, which is believed to have no lead service pipes, revealed lead concentrations as high as 67 $\mu\text{g/L}$ in samples collected at high flow rate, even after several minutes of flushing. The highest lead sample had more than 3000 $\mu\text{g/L}$ zinc, giving a lead/zinc ratio of 2%, similar to that detected in the galvanized steel pipe removed from the system. The sample also contained high levels of iron (22,000 $\mu\text{g/L}$) and detectable cadmium ($> 0.1 \mu\text{g/L}$). Interestingly, the sample also contained 1000 $\mu\text{g/L}$ copper, implying either the presence of brass or that deposition corrosion is occurring. In some cases, lead and zinc concentrations were correlated; in one particular home, samples collected at high flow rate demonstrated a very strong correlation with $R^2 = 0.976$, and the presence of detectable cadmium ($> 0.1 \mu\text{g/L}$) indicated galvanized steel pipe as a lead source.

Role of Flow Rate in Lead Release from Galvanized Steel Pipe. Sequential (profile) sampling at a home in Chicago, IL revealed that lead release from galvanized steel pipe is sensitive to changes in flow rate and removal of the aerator (Figure 5). To put the flow scenarios reported here in the context of consumer water use, the high flow sample with the aerator would be representative of using a kitchen tap at its maximum flow rate, such as when filling a large pot or pitcher. The high flow samples without the aerator are not typical of kitchen use, but represent

the flow rates that can be achieved from non-drinking taps such as Roman bath spouts and laundry room faucets (Clark et al. 2014). This particular home contained multiple lead sources, including both a lead service line and galvanized steel premise plumbing. Despite this, both lead and cadmium concentrations in water were correlated to the zinc concentration in water for all samples collected (Figure 5a), implying that the zinc coating on the premise pipes is a dominant source. Furthermore, when only samples taken at the highest flow rate with the aerator removed are included, the correlation becomes even stronger ($R^2 > 0.90$; Figure 5b). One possible reason for this is the dominance of particulate metal release in these samples (Clark et al. 2014), and it is expected that elevated lead levels in this home are the result of scale being scoured from galvanized steel pipe walls at high flow. For example, the sample with the highest lead concentration (63 $\mu\text{g/L}$, 0% soluble) also contained high levels of particulate zinc (600 $\mu\text{g/L}$, 10% soluble) and iron (1160 $\mu\text{g/L}$, 0% soluble). The particulate copper concentration in this sample was also elevated (44 $\mu\text{g/L}$, 2% soluble), an observation consistent with the scouring of copper-containing deposits from the galvanized pipe wall. This result implies that deposition corrosion could play a role in metal release to water for this home, which was known to have experienced a recent partial lead service pipe replacement with copper.

Household Correlations of Lead, Cadmium, and Zinc at High Flow Rate. Strong correlations between lead, cadmium, and zinc found in Chicago were also present in field samples from Washington, D.C. and Providence, RI (Clark et al. 2014). Of 12 homes with lead service lines sampled in Washington, D.C., five demonstrated a correlation between lead and zinc (> 0.8) at high flow with no aerator (Figure 6). Similarly, 4 out of 12 homes with lead service lines sampled in Providence showed the same correlation ($R^2 > 0.7$; Figure 6a). Correlations were also found between zinc and cadmium, iron, and copper in some homes (Figure 6a). Both

cadmium and iron could be expected if release is due to galvanized steel pipe, and the correlation to copper could be a result of deposition corrosion effects. It is important to note that for many of these homes, galvanized steel was not indicated as a lead source by co-occurrence of cadmium. Only 8% of samples in both Washington, D.C. and Providence contained detectable ($> 0.1 \mu\text{g/L}$) cadmium. Among the samples with non-detect cadmium were several extremely high lead samples ($1800 \mu\text{g/L}$ in Washington, D.C. and $7700 \mu\text{g/L}$ in Providence), which are believed to result from scouring of particles from the lead service line, as well as samples containing high levels of both lead and tin believed to result from dislodged solder particles (Clark et al. 2014).

Lead Release from Galvanized Steel Pipe in Schools. Analysis of results from 92 samples collected from different taps in a Washington, D.C. school did not demonstrate a consistent correlation between zinc and lead or cadmium, as expected given variability in coatings. However, when samples were separated into two groups based on the detection limit for cadmium of $0.1 \mu\text{g/L}$, cadmium $>$ MDL ($N = 44$) and cadmium $<$ MDL ($N = 48$), the detectable cadmium group had an average lead concentration of $194 \mu\text{g/L}$, more than ten times higher than the average lead concentration of the non-detect cadmium group ($18 \mu\text{g/L}$). This result implies that the presence of a galvanized steel pipe, as flagged by the presence of cadmium as a “fingerprint,” is associated with elevated lead in water.

Galvanized Steel Pipe and EBL. In 2008, a case of childhood elevated blood lead (EBL) in Washington D.C. led to water sampling, which revealed extremely high lead levels (nearly $1,000 \mu\text{g/L}$). Further analysis revealed that the concentration of lead in this home, which was known to contain galvanized steel pipe, was highly correlated to the zinc concentration (Figure 7). Furthermore, zinc and cadmium were correlated, the “fingerprint” for lead release from

galvanized steel, implying that galvanized steel pipe contributed a significant fraction of the lead in water in this case.

Relative Importance of Direct and Indirect Lead Release. Although recent work has appropriately drawn attention to galvanized steel pipe as an important source of lead in drinking water (HDR Engineering Inc. 2009; Wasserstrom 2014), the HDR work has focused exclusively on *indirect* release of lead via seeding. While lead “seeding” can and does occur in some cases, it is important to not overlook *direct* release of lead from the zinc coating itself. For galvanized steel pipes harvested from a home in Chicago, IL with a lead service line, which serves as an upstream lead source, a comparison of the concentration of lead on the inside of the pipe compared to the outside can provide insight into the relative contribution of direct and indirect sources of lead release (Figure 8).

The concentration on the outside of the pipe represents the concentration of lead in a new pipe coating available for direct release, while the concentration on the inside reflects residual direct release lead and any seeded lead available for indirect release. In this home, the concentration of lead by weight detected by XRF on the inside of the pipe was never more than 2%, and was on average less than 1%, which is similar to the concentration found on the outside of the pipe (Figure 8). This provides an example of a case where direct release of lead dominates relative to indirect release, and highlights the need to consider both mechanisms when evaluating lead-in-water contributions from galvanized steel pipe.

CONCLUSIONS

Analysis of pipe surfaces, bench scale studies, and field samples for lead leaching from galvanized steel pipe yielded the following conclusions:

- Surface analysis of galvanized steel pipe coatings removed from modern buildings, revealed surface concentrations up to 1.8% lead, which is roughly consistent with the composition of Prime Western Grade zinc.
- Bench-scale tests with harvested galvanized steel pipe revealed concentrations as high as 172 µg/L lead could be released from galvanized steel pipe under dump-and-fill conditions, and that lead and cadmium are correlated to zinc when galvanized steel pipes are the source of lead release to water.
- Samples collected from homes in Washington D.C., Providence, RI, and Chicago, IL, and a city in Florida revealed strong correlations between cadmium, lead, and zinc indicative of galvanized steel as a significant source of lead in these homes.
- The above correlations were strongest at high flow rates, especially without aerators, implying that particulate release from zinc coatings can be the dominant source of lead at these flow rates
- When samples collected at a school in Washington, D.C. were divided into two groups based on a cadmium threshold of 0.1 µg/L (the MDL for cadmium by ICP-MS), the samples with detectable cadmium had an average lead concentration 10X higher than the samples without cadmium, implicating galvanized steel pipe as a significant source of lead in this school.
- Although indirect lead release via lead “seeding” onto galvanized steel pipes can occur under some conditions, considering only this mechanism gives an incomplete picture of lead release from galvanized steel pipe, and the contribution of direct release from the zinc coating to lead in water should be considered when the overall risk of lead exposure from galvanized steel pipes is estimated.

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AUTHOR DISCLOSURE STATEMENT

No competing financial interests exist.

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Appendix B. Electrochemical Reversal

Failure by Pitting and Tuberculation

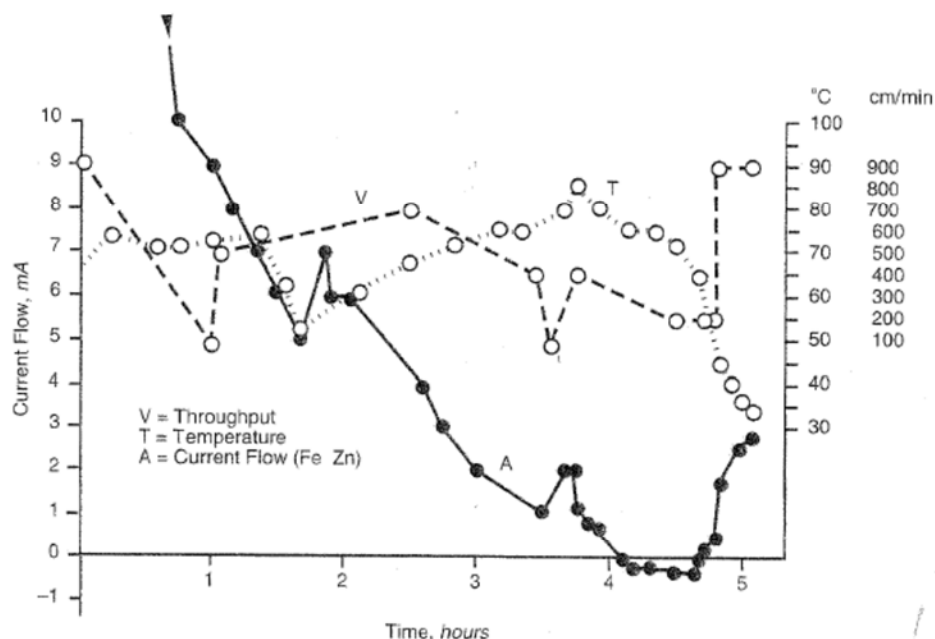
For as long as galvanized pipe has been in use, there has been concern about failure by pitting and tuberculation. Although pitting of galvanized pipe does occur in cold water, pitting in hot water is more common. A great deal of research was done on this subject between 1935 and 1950, and some research has been carried out since then (Schikorr 1939; Kenworthy 1943; Kenworthy and Smith 1944; Gilbert 1948; Hoxeng and Prutton 1949; Hoxeng 1950; Guest 1956; Weast and Shulman 1962; Gouda, Khedr, and Shams El Din 1967; Mihailov and Iovchev 1981; Haney 1982). Probably the majority of this work has discussed the problem in terms of potential reversal, which occurs between zinc and iron (that is, zinc becoming noble with respect to iron) under certain conditions of water quality and temperature. Significant research has also been done on copper-induced pitting, poor quality of manufacture, and galvanic couples. Studies on potential reversal at elevated temperature began because of an interest in pitting problems in water heaters. Also, pitting has, in many instances, been associated with poor-quality manufacturing processes. These four subjects—potential reversal, copper-induced pitting, pitting resulting from poor-quality manufacturing, and pitting or tuberculation by galvanic couples—will be discussed in the following paragraphs.

Pitting as a result of potential reversal. Schikorr (1939) was the first to demonstrate that the relative potentials of zinc and iron can be reversed at higher temperatures. He also demonstrated that the reversal is accomplished primarily by shifts in the potential of the zinc surface and that iron's potential remains relatively stable. Figure 3-24 summarizes some of Schikorr's results, showing the current flow between iron and zinc electrodes (briefly connected for each measurement) and the temperature and velocity during the test. The authors of this chapter have confirmed this phenomenon in their laboratories, as have most of the investigators cited earlier. It has been shown to be a function of water quality, oxygen tension, and temperature.

Perhaps the most thoughtful analysis of this hot-water, potential reversal pitting problem is that of Gilbert (1948), who integrated the work of others with his own to develop an explanation. Gilbert's analysis follows.

In cold water, zinc is normally anodic to steel. Depending on conditions, pitting does sometimes occur, but the compound or alloy layers beneath the eta layer (Figure 3-2) have a more noble potential than does the eta layer itself. As a result, the pits will normally stop once they reach the alloy. Often the pits begin to widen at this point. Because of its more noble potential, the alloy does not offer much protection to the base steel. As a result, the iron will eventually pit, but normally this does not occur until more than half of the surface is corroded to the alloy layer.

In hot water, the surface scale of zinc apparently changes, forming a scale that more effectively supports the reduction of oxygen at the cathode and that "heals" some of the anodic sites, reducing the anodic area. Gilbert suggested that zinc might have a hydroxide scale at low temperatures and a zinc oxide scale at higher temperatures. This process has little effect on the overall corrosion rate of zinc, but the increased polarization of the anodic sites due to their reduced area and the more effective depolarization of the cathodic sites due to the greater conductivity of the new scale substantially increase the potential of the zinc, making it more noble than the iron. As a result, any exposed iron becomes anodic and severe pitting begins. In soft water, no scale is deposited and the pitting attack will continue until the pipe wall is perforated. In hard, scale-forming water, if the conditions are



Source: Schikorr (1939).

Figure 3-24 Potential reversal of iron and zinc in a circulating hot-water loop

particularly severe, perforation may occur rapidly. However, if no failure occurs during these early stages, a scale will be deposited and pitting will be arrested.

In the late 1960s, the ILZRO examined some of the basic assumptions on which Gilbert's model is based (ILZRO 1967). Examining the scale formed on galvanized pipe corroding in distilled water, they found zincite (ZnO), beta zinc hydroxide, and eta zinc hydroxide on the pipe surface. On the surface of the relatively pure zincs, equal amounts of beta and eta Zn(OH)_2 were found in scale formed at temperatures below 5°C , but ZnO dominated at higher temperatures. Tests confirmed Gilbert's suggestion that the zincite formed will serve as a semiconductor.

Unfortunately, these studies were not extended to determine the nature of the scale formed in the presence of the carbonate buffer found in tap water. As discussed earlier, recent work at room temperature (Pisigan and Singley 1985) confirmed the work of ILZRO with distilled water but showed that hydrozincite is dominant in the presence of carbonate. The hydrozincite scale may break down at high temperatures in certain water qualities, leaving a zincite scale and facilitating the mechanisms described by Gilbert.

A number of factors influence the potential reversal phenomenon. First, oxygen must be present. Without oxygen, cathodic polarization is limited by the hydrogen overpotential and the potential of the zinc surface remains active with respect to the iron. Gilbert noted that the zinc potential is influenced by chloride, sulfate, and bicarbonate. Chloride and sulfate decreased the potential of the zinc, making polarity reversal less likely; bicarbonate ennobled the zinc, enhancing reversal. Studies by others (Hoxeng and Prutton 1949; Hoxeng 1950; Gouda, Khedr, and Shams El Din 1967; Haney 1982) confirmed this information and also established that potentials can be reduced by calcium and silicates and increased by the addition of

monobasic sodium phosphate. Gouda, Khedr, and Shams El Din demonstrated that the influence of the aggressive ions (chloride and sulfate) on the potential of the zinc surface could be described by the following relationship:

$$E = a - b \log (C)$$

Where:

C = the concentration of the ion

Generally, the behavior of these ions is consistent with Gilbert's model of the process. Aggressive ions like chloride and sulfate would continue to attack the anodic sites, maintaining larger anodic areas at higher temperatures. Calcium, bicarbonate, carbonate, and silica would be expected to maintain an active potential on the zinc surface by laying a calcium or silicate scale on the cathodic sites, preventing the more rapid depolarization of oxygen even though the nature of the zinc scale itself may become more conductive.

Kruse (1983) provided a complete summary of the hot-water pitting problem. Results reviewed by Kruse indicated that ennobling can occur at temperatures as low as 35°C and that the problem of potential reversal is highly dependent on water quality. In response to these problems, the Germans limit the use of galvanized steel pipe to applications in which the temperature is less than 60°C (DIN 50930).

